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# PATENT SPECIFICATION

DRAWINGS ATTACHED

Inventor: REX EVERETT LIDOV

1,088,009



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Date of Application and filing Complete Specification: Nov. 3, 1964.

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## ERRATA

SPECIFICATION No. 1,088,009

Page 1, line 38, for "duration" read "destruction"

Page 3, line 46, for "is" read "it"

Page 3, line 97, for "21" read "31"

Page 4, line 16, after "through" delete "the"

Page 4, line 24, for "discharge" read "discharged"

Page 5, line 26, for "cases" read "case"

Page 5, line 76, after "introduced" insert "adjacent"

Page 5, line 106, after "of" delete "the"

THE PATENT OFFICE

20th November 1967

15 particularly it relates to such processes and apparatus wherein the reaction is carried out in an elongated reactor maintained under temperature control by indirect heat exchange between the gaseous reaction mixture and a heat-transfer fluid flowing externally of the reactor.

20 Many processes for the catalytic vapour phase partial oxidation of organic materials are known and many of these are carried out in elongated tubular reactors arranged in a tube and shell heat exchanger system so that the heat of reaction may be removed. In 25 many of these, the oxidation reaction produces a relatively localized very high temperature zone from which heat must be removed at a very rapid rate if temperature control is to 30 be maintained. This very high temperature zone is caused by the fact that much of the desired oxidation reaction takes place at a very rapid rate in or over a very short portion of the reactor tube length. Failure to 35 control reaction temperature in this high temperature zone leads to loss through complete duration of the organic material by over-oxidation. Accordingly, it is necessary to circulate coolant very rapidly and at a suitably 40

the heat available in the hot-spot zone of the reactor and the remainder of the reactor can, of course, be solved by separating these zones and using a multi-reactor system, thus providing each reactor section with coolant at that temperature and in such amount as is best suited to it. While theoretically, this is an ideal system, practically, it is uneconomic; the increase in product yield obtained does not justify the very large expenditures required to provide and operate a multiplicity of reactors and coolant circulation systems. The art requires some resolution of the described difficulties within the framework of the commercially useful single reactor system dictated by chemical process economics.

According to the invention a process for the catalytic vapour phase oxidation of an organic compound in an elongated reactor surrounded by a heat-transfer zone through which a heat-transfer fluid flows from an inlet at one end to an outlet at the other end, includes the improvement which comprises controlling the temperature as required at different points along the reactor by adding heat-transfer fluid to the heat-transfer zone

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Int. Cl.: —B 01 j 9/00

## COMPLETE SPECIFICATION

### Process and Apparatus for the Vapour Phase Oxidation of Organic Compounds

- We, HALCON INTERNATIONAL INC., 2, Park Avenue, New York 16, New York, United States of America, a corporation organized and existing under the laws of the State of Delaware, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us and the method by which it is to be performed, to be particularly described in and by the following statement:—
- THIS INVENTION relates to processes and apparatus for the catalytic vapour phase partial oxidation of organic compounds. More particularly it relates to such processes and apparatus wherein the reaction is carried out in an elongated reactor maintained under temperature control by indirect heat exchange between the gaseous reaction mixture and a heat-transfer fluid flowing externally of the reactor.
- Many processes for the catalytic vapour phase partial oxidation of organic materials are known and many of these are carried out in elongated tubular reactors arranged in a tube and shell heat exchanger system so that the heat of reaction may be removed. In many of these, the oxidation reaction produces a relatively localized very high temperature zone from which heat must be removed at a very rapid rate if temperature control is to be maintained. This very high temperature zone is caused by the fact that much of the desired oxidation reaction takes place at a very rapid rate in or over a very short portion of the reactor tube length. Failure to control reaction temperature in this high temperature zone leads to loss through complete duration of the organic material by over-oxidation. Accordingly, it is necessary to circulate coolant very rapidly and at a suitably low relative temperature to remove the heat through the limited tube surface area available in the zone of rapid reaction. In consequence, the greater length of reaction tube which follows the above described "hot-spot" zone is cooled excessively. The relatively slow oxidation reaction which continues as the reactants move through the tube cannot supply heat sufficiently rapidly to maintain, in the remainder of the reactor, as high a temperature as is desirable efficiently to complete the partial oxidation. As a result, yields suffer. The problems posed by the somewhat contradictory coolant requirements of the "hot-spot" zone of the reactor and the remainder of the reactor can, of course, be solved by separating these zones and using a multi-reactor system, thus providing each reactor section with coolant at that temperature and in such amount as is best suited to it. While theoretically, this is an ideal system, practically, it is uneconomic; the increase in product yield obtained does not justify the very large expenditures required to provide and operate a multiplicity of reactors and coolant circulation systems. The art requires some resolution of the described difficulties within the framework of the commercially useful single reactor system dictated by chemical process economics.
- According to the invention a process for the catalytic vapour phase oxidation of an organic compound in an elongated reactor surrounded by a heat-transfer zone through which a heat-transfer fluid flows from an inlet at one end to an outlet at the other end, includes the improvement which comprises controlling the temperature as required at different points along the reactor by adding heat-transfer fluid to the heat-transfer zone

and/or removing heat-transfer fluid from the heat-transfer zone at one or more intermediate points along the zone.

5 In this way the temperature of various parts of the reactor along its length may be controlled independently of variations in heat flow produced by the reaction as it occurs along the length of the reactor, for example by increasing the amount of coolant heat-transfer fluid where more heat is evolved by the reaction and decreasing the amount where less heat is evolved. Thus in one procedure according to the invention substantially all of the heat transfer fluid is fed into the heat-transfer zone at the inlet whereas it is removed from the zone at the outlet and one or more intermediate points.

20 The process of the invention may be applied with advantage to oxidations in which a hot spot is formed and in such case the reaction zone may be maintained at a gradually decreasing temperature gradient beyond the hot spot in the direction of flow of the reaction mixture, an improved conversion being obtained in this manner. The temperature gradient may be step-wise.

25 Substantially all of the heat-transfer fluid may be introduced adjacent the hot spot and allowed to flow past the hot spot, part of the fluid being removed adjacent to the hot spot on the other side and the remainder at one or more points relatively remote from the hot spot.

30 The process of the invention may be applied to the partial oxidation of a phthalic anhydride precursor to produce phthalic anhydride. Thus it may be applied to the oxidation of naphthalene with atmospheric air at a series of temperatures in the range of 350° to 550° C. or to the oxidation of o-xylene with atmospheric air at a series of temperatures in the range of 425° to 650° C.

35 In the process of the invention the temperature of heat transfer fluid added to the reactor at various intermediate points, may be changed from that of the bulk of the heat transfer fluid by means external to the reactor, before the fluid is added to the reactor.

40 The invention includes a process for the catalytic partial oxidation of an organic vapour in an elongated reactor in which process the volume of the circulating coolant, required to remove exothermic reaction heat, is changed at various intermediate points along the length of the reactor, said changes being effected to ensure maximum cooling in the zone of most rapid heat evolution and reduced cooling in zones of reduced heat release, in order to maintain and control temperatures through the length of the reactor.

60 The process of the invention may be carried out using

(i) a down-flowing reactant and a down-flowing coolant;

(ii) a down-flowing reactant and an up-flowing coolant; 65

(iii) an up-flowing reactant and an up-flowing coolant;

(iv) an up-flowing reactant and a down-flowing coolant; 70

The invention also includes apparatus for use in the catalytic, vapour phase partial oxidation of an organic compound, comprising an elongated reactor and a jacket forming an enclosed zone surrounding the reactor and adapted to permit the flow of a heat-transfer fluid in indirect thermal contact with the reactor from an inlet at one end of the zone to an outlet at the opposite end, the zone being provided with one or more baffles dividing it into communicating compartments spaced along the length of the reactor and having at least one additional inlet and/or outlet at an intermediate point along the zone for the addition and/or removal of heat-transfer fluid to and/or from the zone. 75

Preferably, each compartment of the zone has either an inlet or an outlet for heat-transfer fluid into or out of the zone. The apparatus may be in cylindrical tube and shell form wherein the region between the tubes and the shell is divided into a plurality of cylindrical sections. 80

The accompanying drawing illustrates one embodiment of the invention, partially in elevation and partially in section. 85

The invention is illustrated by the following examples, in which parts and percents means parts and percents by weight, respectively, unless otherwise indicated. 90

#### EXAMPLE 1

Referring to the accompanying drawing, a feed mixture of air and naphthalene is passed via inlet 10 into reaction apparatus 11. This apparatus is provided with a header 13, reactor tubes 15 loaded with catalyst 16, outlet header 17 and reaction product outlet 18. In addition, the apparatus is provided with a series of baffles 35a, 35b, and 35c, at right angles relative to the tubes which divide the region between the outer shell or wall 36 and the tubes into a series of sections, 40, 41, 42 and 43. Each of the sections is provided with one or more coolant inlet or outlet means 20, 22, 24 and 26, 28, 30, 32 and 34 provided with valves 19, 21, 23 and 25, 27, 29, 31 and 33 respectively. Each reactor tube is provided with a suitable known catalyst loaded in usual manner, and the tubes may be provided with known temperature sensors (thermocouples) arranged therealong or therein in known manner (not shown). 105

The flow of coolant which, in this case, is molten salt is regulated so as to control temperature in the "hot-spot" zone and, at the same time to maintain as high a temperature in the remainder of the reactor tube as is 120 125



desirable. The feed to each reactor tube contains one part by weight of naphthalene to about thirty parts by weight of air; it is preheated to about 250° to 350° C., i.e., to just below reaction temperature, in known manner. Under these circumstances, a hot-spot develops at about the junction between section 40 and section 41. The minimum coolant temperature permissible is about 250° to 350° C., again, about the minimum reaction temperature. A coolant any colder than this temperature will cool incoming gases below reaction temperature and no reaction will occur. Thus, in order to control the hot-spot or "hot-zone" temperature, coolant at this minimum temperature is introduced through line 28 and valve 27. If the hot-zone temperature is to be adequately controlled, the amount of coolant introduced must be such that its temperature rise, as it passes through the hot zone, is not more than a few degrees. All of the coolant is introduced through line 28 and valve 27 because the fluid, at initiating reaction temperature, is an economical means for bringing the reaction gas to that temperature. Under these conditions, the hot-spot zone can be maintained in the range of about 550° to 600°C. without undue difficulty. Valve 19 is kept closed. However, valve 29 is opened to such an extent that approximately 90 to 95% of the molten salt entering through line 28 is discharged from the reactor through line 30. By discharging most of the coolant in this fashion it is possible to hold reaction temperature in zone 42 appreciably above the temperature of the coolant entering that section past baffle 35b. The remainder of the coolant is finally discharged through valve 33 and line 34. The reaction mixture is processed after leaving the reactor tubes, in known manner to recover phthalic anhydride. There is thus obtained a very high yield of phthalic anhydride of exceptional purity.

The feed may contain 1 part by weight of naphthalene to about 30 parts by weight of air, and is may be preheated to about 250° to 350°C., i.e., to just below reaction temperature in known manner. The catalyst bed is raised to initial reaction temperature in known manner and then after the zone of initial high temperature is passed, maintained at a gradually decreasing reaction temperature down to about 350°C. at or near the reactor outlet. The reaction is exothermic and the flow conditions are maintained so that the most rapid reaction is in the initial part or section of the reactor tubes, and the more rapid flow of coolant is maintained around this section of the reactor tubes.

Generally a plurality of reaction tubes is used, and a known vanadium oxide type catalyst provided with a suitable support may be used. Although four reaction zones or sections are shown, arranged for an optional zig-zag

flow, a larger or a smaller number may be used if desired as may different flow paths. A plurality of inlet or outlets or coolant lines for each zone may be used and these may be spaced in any convenient manner. In addition, vertical or other baffle means may be used more evenly to distribute the flow of coolant through or across each section or zone.

If desired, the horizontal baffles which separate the zones may be provided with perforations for upward or downward flow of coolant from one zone to the other in order to help smooth out the temperature gradient.

A loose fit between the tubes and the horizontal baffles permits such downward or upward flow, also with suitable regulation of the inlet and outlet valves.

Instead of naphthalene, other known phthalic anhydride precursors may be used, such as substituted naphthalene and the like, and similar results are obtained therewith.

#### COMPARATIVE EXAMPLE A

The above example is repeated except that the coolant is caused to flow through the reactor in the fashion now used by the art when employing single reactors with co-current flow of the circulating heat abstracting medium. This is accomplished by introducing all of the coolant, as in Example 1, in the same amount and at the same temperature, through valve 27 and line 28. However, in this case, valves 19, 21, 23, 25, 29 and 31 are kept tightly closed and no coolant leaves the reactor at intermediate points. Instead the entire flow is discharged through valve 33 and line 34. As a result, the reaction temperature drops sharply immediately the hot zone at the junction of sections 40 and 41 is past, and only that very limited amount of oxidation which could take place at about the relatively low temperature of the coolant continues outside the hot zone.

The yield of crude phthalic anhydride recovered is not only lower than in the case described in Example 1, but, in addition the anhydride is less pure. It is contaminated with large amounts of dark tarry substances and other impurities compared to the material recovered in Example 1 and is in consequence, much more difficult to refine. These tarry substances and other impurities are present in and contaminate the product because the lower temperature obtaining in the reactor tubes in the reactor operated in accordance with current art practice prevents conversion of these materials to useful products or their removal by complete oxidation.

#### EXAMPLE 2

The Example 1 procedure is repeated except that the feed is benzene with air and the reaction system is arranged in known manner for the production of maleic anhydride and

analogous improvements in the yield and quality are obtained.

#### EXAMPLE 3

5 The procedure of Example 1 is repeated except that o-xylene is converted to phthalic anhydride at temperatures in the range of 425° to 650°C., the analogous improvements in the yield and quality are obtained.

#### EXAMPLE 4

10 The process of Example 1 is repeated with two essential modifications; the oxidizable organic material employed is durene (1,2,4,5-tetramethylbenzene) rather than naphthalene and the coolant flow is further modified. As  
15 already described, the volume of coolant entering the reactor through the valve 27 is regulated to maintain the hot-zone at the desired maximum temperature (550 to 600° C.); the temperature at which it is introduced into the reactor is as previously explained, determined by the minimum temperature required to initiate oxidation (200 to 300°C). Again, as earlier described, 90 to 95 percent of the coolant is discharge  
25 through valve 29 and line 30. In this case, however, it is found desirable to divert an additional amount of coolant through valve 25 and line 26 in order to maintain even higher temperatures in section 43 than would  
30 otherwise be obtained. To accomplish this purpose valve 25 is opened sufficiently so that an amount of coolant roughly equivalent to about 90 percent of that flowing through reactor section 42 is discharged. Accordingly,  
35 only about one half to one percent of the coolant flow originally introduced into the reactor through line 28 is finally discharged through valve 33 and line 34. When the coolant flow is such as here described, the  
40 yield of pyromellitic anhydride obtained is appreciably higher than when the path of the coolant is that described in Example 1.

In all cases, of course, the coolant may be processed in known manner to recover heat  
45 therefrom and may subsequently be recycled.

The invention has been described for reactors in which the flow of reactants is in a downward direction and in which the coolant flows in the same direction or co-currently.  
50 An equivalent modification of a counter-current coolant flow as the latter is now employed is possible. Thus, with the reactant flow as earlier described, counter-current coolant flow would require that the coolant, in the  
55 reactor described, be introduced through valve 33 and line 34. To obtain the advantage previously described, the amount of coolant so introduced need be only a minor proportion of the amount ultimately needed to maintain  
60 temperature control in the hot-spot zone higher in the reactor. In order to aid in maintaining temperature, additional amounts of coolant may either be added or removed

through valves 25, 23 and 31. In any event, and assuming, that in this case, too, the hot  
65 spot zone lies in sections 41 and 40, the amount of coolant required to control hot-spot temperatures is finally added through valves 29 and, if desired, 21. All coolant, is, of course, discharged through valves 27 and  
70 19.

Reactors of the type described are sometimes operated so that the reacting gases flow upwardly through the reactor. In such cases, too, coolant flow is preferred by some to be  
75 co-current and by others to be counter-current to the direction of the gas flow. In either case, the methods to be employed to obtain maximum cooling through the hot spot zone (which in a reactor in which the  
80 reactants flow upwardly will be in the lower half of the reactor) and reduced but controlled amounts of cooling in the remainder of the reactor will, *mutatis mutandis*, be readily evident to those skilled in the art  
85 from descriptions already detailed herein.

It is also possible, as may already be evident from what has been said, to alter the temperature of the relatively small volumes of temperature control fluid being added to  
90 the reactor at the various intermediate points by causing the fluid to pass through appropriately sized heat exchange units before passing into the reactor. The relatively small volume of fluid which requires heating or  
95 cooling makes such a possibility economically feasible. Thus, for example, in order to reduce the volume of coolant which must be circulated when the temperature thereof is no lower than the minimum initiation temperature of the oxidizing gas mixture, in the  
100 situation as described in Example 1, it is only necessary to add molten salt through valve 21 and line 22 which is at a temperature below the coolant added through line 28. Since  
105 the oxidation has already been well started by the time the gas passes through section 40 of the reactor and is proceeding exothermically with the evolution of large amounts of heat, it need no longer be feared that the  
110 addition of coolant through line 22 which is below the minimum initiation temperature of the reaction will prevent the oxidation from starting. The total flow of coolant required will, when this alternative is employed, be dependent on the temperature of  
115 the fluid added at line 22, but in any event, the sum of the amount added through lines 28 and 22 will be less than if all of the coolant had been added through line 28, provided only  
120 that the coolant added through line 22 is below the temperature of the minimum permissible through line 28. Similarly, if higher temperatures than can conveniently be maintained simply by reducing the flow of coolant are  
125 desired in the lower sections of the reactor, small amounts of the heat-transfer fluid heated in any suitable and known manner

by means external to the reactor can be added at any of the intermediate points provided.

5 All of these highly flexible alternatives for controlling temperatures at various points in the reactor are possible without any modifica-  
 10 tions of the usual single stage reactor normally employed beyond that required by the addition of inlet-outlet ports and suitable valves at various points. Moreover, in general,  
 15 little modification of heat transfer fluid circulation loops normally provided is necessary. However, as already indicated, the addition of relatively small exchangers for further altering the temperature of small amounts  
 20 of the circulating fluid introduced at various points in the reactor may further increase the precision of control thus made available by this invention.

25 The means here described for increasing the precision and range of temperature control in simple single stage reactors used for carrying out exothermic reactions requiring that large amounts of heat be removed are, of course, independent of the absolute tem-  
 30 peratures at which the reactors are used in given cases or, of the various ranges of temperatures needed in any given case. The modifications and operating methods disclosed will serve equally well for all kinds of reactions  
 35 of the type recited. Moreover, it will be evident to those skilled in the art that with simple changes, immediately evident now that the broad methods for temperature control here disclosed have been described, the same reactor modifications and processing methods  
 40 will be applicable to endothermic reactions which require the addition of heat as the reaction proceeds.

45 This invention provides means for altering the hitherto fixed relationship between the amount (and temperature) of coolant in various zones of a single reactor so that differing requirements for coolant in the various zones can be satisfied.

#### 45 WHAT WE CLAIM IS:—

50 1. In a process for the catalytic vapour phase partial oxidation of an organic compound in an elongated reactor surrounded by a heat-transfer zone through which a heat-transfer fluid flows from an inlet at one end to an outlet at the other end, the improve-  
 55 ment which comprises controlling the temperature as required at different points along the reactor by adding heat-transfer fluid to the heat-transfer zone and/or removing heat-transfer fluid from the heat-transfer zone at one or more intermediate points along the zone.

60 2. A process as claimed in claim 1 in which the heat-transfer fluid is fed into the heat-transfer zone only at the inlet and is removed therefrom at the outlet and one or more intermediate points spaced along the zone.

3. A process according to claim 1 in which a 'hot spot' zone exists in the reactor and in which the reaction zone is maintained at a gradually decreasing temperature gradient beyond the hot spot zone in the direction of flow of the reaction mixture, whereby improved conversion is obtained. 65 70

4. A process according to claim 3 wherein the temperature gradient is step-wise.

5. A process as claimed in claim 3 or 4 in which substantially all the heat-transfer fluid is introduced to the hot spot of the reactor and flows past the hot spot, a part of the heat-transfer fluid is removed adjacent to the hot spot and the remainder of the heat-transfer fluid is removed when relatively remote from the hot spot. 75 80

6. A process according to any of the preceding claims wherein the organic starting material is a phthalic anhydride precursor.

7. A process according to claim 6 wherein naphthalene is oxidized by atmospheric air at a series of temperatures in the range of 350° to 550°C. 85

8. A process according to claim 6 wherein *o*-xylene is oxidized by atmospheric air at a series of temperatures in the range of 425° to 650°C. 90

9. A process according to any of the preceding claims in which heat transfer fluid is added to and removed from the reactor at various intermediate points and in which the temperature of the fluid so added is changed from that of the bulk of the heat-transfer fluid by means external to the reactor, before the fluid is added to the reactor. 95 100

10. A process according to claim 1 in which the volume of the circulating coolant, required to remove exothermic reaction heat, is changed at various intermediate points along the length of the reactor to ensure maximum cooling in the zone of the most rapid heat evolution and reduced cooling in zones of reduced heat release, in order to maintain and control reaction temperatures through the length of the reactor. 105 110

11. A process according to any of the preceding claims using a down-flowing reactant and a down-flowing coolant.

12. A process according to any of claims 1 to 10 using a down-flowing reactant and an up-flowing coolant. 115

13. A process according to any of claims 1 to 10 using an up-flowing reactant and an up-flowing coolant.

14. A process according to any of claims 1 to 10 using an up-flowing reactant and a down-flowing coolant. 120

15. A process for the catalytic partial oxidation of an organic compound in the vapour phase substantially as herein described and exemplified. 125

16. An oxygen-containing organic product when produced by the process of any of the preceding claims.



17. Apparatus for use in the catalytic vapour phase oxidation of an organic compound, comprising an elongated reactor and a jacket forming an enclosed zone surrounding the reactor and adapted to permit the flow of a heat-transfer fluid in indirect thermal contact with the reactor from an inlet at one end of the zone to an outlet at the opposite end, the zone being provided with one or more baffles dividing it into communicating compartments spaced along the length of the reactor and having at least one additional inlet and/or outlet at an intermediate point along the zone for the addition and/or removal of heat-transfer fluid to and/or from the zone.
18. Apparatus as claimed in claim 17 in which each compartment has an inlet or an outlet for passage of heat-transfer fluid into or out of the zone.
19. Apparatus according to claim 17 or 18 comprising a plurality of parallel elongated reaction tubes spaced apart and a common jacket forming an enclosed cylindrical zone surrounding the tubes and having its axis parallel to the axes of the reaction tubes, the zone being divided by one or more baffles perpendicular to the axis of the tubes into communicating cylindrical compartments.
20. An apparatus for use in the catalytic vapour phase oxidation of an organic compound substantially as hereinbefore described with reference to the accompanying drawing.

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1088009

COMPLETE SPECIFICATION

1 SHEET

This drawing is a reproduction of  
the Original on a reduced scale

